

EXPERIMENTAL OBSERVATIONS CONCERNING THE TWO-COMPONENT CONCEPT OF COAL STRUCTURE

by

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Abstract

The hypothesis that coals can be considered to consist of two component groups has its origins in observations of coal behaviour as well as deriving from the analysis of coals and attempts to define their structure. The results of extensive studies of untreated, preheated and hydrogenated coals, using analytical and microscopic techniques, have allowed some insight into the association between the so-called mobile phase and macromolecular network, and have provided information upon differences in their chemical properties.

The yield of chloroform-soluble extract has been used to indicate the extent of the mobile phase. In untreated coals, only a portion of the mobile phase is readily removable. After mild preheating or mild hydrogenation, there are sharp increases in the yield of extract and accompanying changes in properties. Under these conditions, it is believed that weak binding between the mobile phase and network is disrupted. The solubilisation of the network requires much higher energy input and necessitates the consumption of hydrogen. The properties of the network components differ significantly from those of the mobile phase and both are coal rank-dependent.

Introduction

Much of the research pursued jointly by the authors and their associates has involved studies of the catalytic hydrogenation of coals in the absence of solvent. The aims have been to utilise this technique to try to elucidate the mechanisms of catalytic coal liquefaction and simultaneously to provide some insight into coal structure. The concept that, in broad terms, coals can be considered to consist of two distinct groups of constituents has been a particular focal point. The hypothesis is not new and has been advanced in a number of ways since the early part of this century. Its revival in recent years is largely attributable to the efforts of the late Peter Given to whom is also owed the now wide usage of the expressions 'mobile phase' and 'macromolecular network' (1,2).

To allow some clarification for a general readership, brief definitions of these terms will be attempted. The mobile phase comprises the smaller molecules in coals, some of which are extractable in solvents. The insoluble portion of coal is primarily a three-dimensional cross-linked macromolecular network or matrix. The mobile phase is attached to or held with the network by physical constraints and weak chemical bonds.

Peter Given was directly instrumental in providing the initiative and impetus which originated the authors' research. These efforts have extended since 1983. Previous findings were disseminated through several publications (3-7). In this paper, some of the earlier data have been collated with more recent (8) and hitherto unpublished results to provide an account of the relevance of these studies to the two-component concept.

Experimental

Coals covering a range of rank downwards from low-volatile bituminous were examined in solvent-free catalytic hydrogenation over the temperature range 300-400°C and for reaction times up to 60 min. The work discussed here specifically involved four coals which were obtained from the Penn State Coal Sample Bank. These were a subbituminous coal (PSOC-1403) and three hvAb bituminous coals, PSOC-1168, PSOC-1266 and PSOC-1510. Characteristics of the coals are summarised in Table 1. The reactors were of the tubing bomb type and the initial (cold) hydrogen pressure was 7 MPa. A sulphided Mo catalyst was introduced to the coal by impregnation from an aqueous solution of ammonium tetrathiomolybdate.

The gaseous products, chloroform-soluble extracts and chloroform-insoluble residues were characterised using a range of analytical techniques. A particular advantage of conducting the hydrogenation reactions in the absence of solvent is that microscopy can be used to observe directly the changes wrought in the whole reacted coals and in the extracted residues. Considerable emphasis was placed on this method of analysis using both visible light microscopy and quantitative fluorescence microphotometry. Detailed descriptions of the procedures and techniques have been given earlier (3-7).

Results and Discussion

Catalytic Hydrogenation

Detailed examinations of the composition and distribution of the reaction products over a range of reaction conditions showed that the four coals exhibited certain common trends. Of particular note, there was in each case, a sharp distinction between the events which took place at low and high conversions. The division occurred at a chloroform-solubles yield of approximately 25% wt dmmf coal.

Low extract yields were obtained either by short reaction times at high temperatures or by more extended reaction at low temperatures. The designations of high and low temperature depend upon the individual coal and, more especially upon the coal rank. The evidence accrued in this research has shown that there exists a threshold temperature below which the potential for liquids formation is minimal and above which conversion can proceed at an appreciable rate.

It is supposed that this temperature is essentially determined by the density and nature of the crosslinks in the macromolecular network. This is consistent with evidence showing that the ease of conversion and the selectivity to lower molecular weight liquids increases with decreasing coal rank (8,9). For the subbituminous coal, the rate of liquids formation was negligible at 300°C and became appreciable at 350°C and higher. The bituminous coals began to

respond only at temperatures around 400°C. Similar observations have been made in experiments which compared the solvent-free hydrogenation of a lignite and a bituminous coal (10).

During the initial stages of conversion, as the liquid yield increased there were radical changes in the properties of the chloroform-soluble extracts. The H/C atomic ratio, aliphatic hydrogen content and oil to asphaltene (O/A) ratio each increased rapidly at first, passed through a maximum and decreased equally precipitately to a lower value, as illustrated in Figure 1. The curve shown for the O/A ratio is typical of the behaviour exhibited by the other coals.

A notable distinction was that the magnitudes of the changes were different for the subbituminous coal and the group of bituminous coals. Examples of the differences between the values for the parent coal extracts and the maxima are: H/C ratio 1.46 to 1.60 for the subbituminous coal, PSOC-1403, and 1.01 to 1.06 for the bituminous coal, PSOC-1266; O/A ratio 0.8 to 8.0 for PSOC-1403 and 0.25 to 1.5 for PSOC-1266.

At the maxima, ^1H n.m.r. and elemental analyses showed that the greater proportion of the extract hydrogen was aliphatic: 10.5% for PSOC-1403 and 6.9% for PSOC-1266. In all cases over 90% of the total hydrogen content was aliphatic at this point. The high aliphatic hydrogen content was associated with the presence of polymethylene chains. The early release of paraffinic material, as n-alkanes and as long chain substituents to aromatic structures, under conditions of mild pyrolysis has been observed in other research (11-13). Over the initial period of conversion, it was also observed that only small quantities of light hydrocarbon gases were produced.

For the four coals, the maxima occurred between 5-10% wt extract yield and the subsequent decreases were arrested between 20-35% extract yield. No distinction could be made on the basis of coal rank although, admittedly, the number of coals is small.

The production of extract yields in excess of 20-35% wt marked the second stage of conversion. Over this period, the H/C atomic ratio and the total aliphatic hydrogen content remained approximately constant or decreased only gradually while the O/A ratio passed through a shallow minimum, Figure 1. The secondary gain in selectivity to oils at high conversions may represent the interconversion of asphaltenes to oils after extended reaction of the primary dissolution products. Other phenomena associated with the progress of the second stage were that the production of light hydrocarbon gases increased, the aromaticity of the extract progressively increased and oxygen functionalities were eliminated.

The consumption of gaseous hydrogen mirrored the changes described above, Figure 1. For the bituminous coals at 400°C, the initial rate of hydrogen uptake was very low. With further reaction, it accelerated, passed through a maximum, and then fell to a lower, more steady value. After about 60 minutes reaction, the total consumption was about 1.5% wt dmmf coal (about 2.0% wt for the subbituminous coal). At the point of transition from the slow initial rate to the accelerating rate, the liquid yields were between 5-15% wt dmmf coal. The acceleration in hydrogen uptake coincided with the end of the first phase of conversion. At this juncture, the total hydrogen consumed was 0.1-0.2% wt. The corresponding figure for the subbituminous coal was about 0.3% wt.

The existence of two stages of conversion has been separately demonstrated in studies by Mobil R & D Corporation where, in non-catalytic solvent liquefaction, two kinetic regimes were distinguished. Initial conversion was rapid with low attendant hydrogen consumption while subsequent conversion was slower and created a much greater demand for hydrogen (14). These findings were re-confirmed in later studies by the same group, when it was further shown that the products first formed were of higher H content and more aliphatic than those generated in the second regime. A subbituminous coal was found to consume more hydrogen than a bituminous coal at the same level of conversion (15).

The foregoing observations have direct implications to coal structure. In the present work, the production of liquids is facile below about 15% liquids yield and requires little hydrogen consumption. The processes most probably involve the release of species which are physically trapped or are weakly bonded to the insoluble matrix. At high conversions, the products are derived from the breakdown of the macromolecular network. This phase of conversion requires the cleavage and stabilisation of strong bonds, thereby creating an appreciable demand for hydrogen.

The products formed during the two stages are quite different in composition which can account for the rather dramatic swings observed in the extract properties with increasing conversion. The hydrogen-rich aliphatic products, which are first liberated, are responsible for the initial increases in the measured parameters. Later, as they become progressively diluted by more aromatic materials emanating from the network, the properties pass through a maximum and then decrease.

Fluorescence Microscopy

The phenomenon of vitrinite fluorescence has been described for 76 humic and vitrinitic materials with levels of organic maturation ranging from peat to low volatile bituminous coal (5,6). Figure 2a shows that fluorescence intensity decreases sharply through the series peat - peat/lignite transitional materials - lignite - subbituminous coal. The so-called primary fluorescence within this range is believed to be due to the presence of fluorophors derived from biopolymers, especially lignin. A second peak in fluorescence intensity (Fig. 2b) commences at about subbituminous rank, is reached in coals with a vitrinite maximum reflectance of about 0.9%, and is largely lost by medium volatile bituminous rank. This "secondary fluorescence" is attributed mainly to the presence of the mobile phase, a conclusion which is supported by a notable parallelism among the trends, in this rank range, of fluorescence intensity, chloroform-solubles yield and Gieseler maximum fluidity (5). The spectral distributions of the secondary fluorescence undergo a red shift due to the increasing conjugation of double bonds which accompanies coalification.

After chloroform extraction, coals still demonstrate low levels of residual fluorescence (Fig. 3), interpreted as being due to entrapped portions of the mobile phase. The figure also shows that mild thermal pretreatment (350°C for 3 min; N₂ atmosphere) considerably enhanced the intensity of fluorescence which subsequently was entirely removed by extended chloroform extraction (6). Apparently the heat treatment disrupts the bonding between network system and mobile phase, resulting in increased yield; with reduced energy transfer between the two phases, there is less possibility for intermolecular quenching, so that fluorescence intensity is enhanced.

Brown and Waters (16) showed that the yield of chloroform-soluble extract could be increased several-fold by coal pretreatment which involved rapid heating and cooling. The liberation of additional extract by this means is identical to the situation described above. The enhanced yields reported by Brown and Waters are of the same order as those corresponding to the initial conversion stage in the catalytic hydrogenation experiments. As this first stage incurred little or no net consumption of hydrogen external to the coal, it is believed that the effects of preheating and of low severity catalytic hydrogenation are equivalent. Brown and Waters concluded that the material derived by preheating was originally present as such in the coals and was not a product of pyrolysis. This is more or less the same definition of the mobile phase as it is understood in the present research.

Just as the untreated bituminous coals showed a parallelism among chloroform-solubles, vitrinite fluorescence intensity and Gieseler plasticity, the products of a single hvAb coal (PSOC-1510), hydrogenated for varying reaction times with a sulfided molybdenum catalyst, showed similar interrelations (Fig. 4). These results, together with the observation that chloroform-extracted coals lose their capability to become thermoplastic (17), are convincing evidence that the mobile phase is a necessary agent in promoting fluid behaviour.

Chloroform extraction of the whole products of dry hydrogenation (400°C; 60 min; 5% Mo; 7 MPa H₂) of PSOC-1266 produced a strongly fluorescent extract and non-fluorescent residue. After drying, the extract was seen under the microscope to contain two components with distinctive fluorescence characteristics (Fig. 5). Component 1 had a fluorescence spectrum very similar to that of the oil (hexane-soluble) fraction of the same hydrogenation products; component 2 had a spectrum like that of the corresponding asphaltene fraction, which, in addition to a higher peak wavelength, had a very much lower fluorescence intensity than the oil fraction. The observed differences in the fluorescence characteristics of the oil and asphaltene fractions are believed to be due to the more highly condensed materials which constitute the latter.

As reaction conditions became more severe, the fluorescence spectra of the hydrogenated vitrinite underwent a red shift (Fig. 6) from around 600 nm at 350°C to around 680 nm at 400°C. The trend is believed to be due to the production of a higher proportion of asphaltenic material from the vitrinite network, as shown earlier by the reduction in O/A ratio with increasing conversion.

Synopsis

The liquefaction behaviour to the four coals investigated allows a general definition of the mobile phase as that material which is readily liberated by mild thermal treatment. The mobile phase components are richer in hydrogen and significantly more aliphatic than the structural units which comprise the network. The latter are connected by much stronger bonds, necessitating more severe reaction and higher hydrogen consumption to secure their release. The compositions of the mobile phase and network are also dependent upon coal rank.

Fluorescent light microscopy allowed a distinction between the extractable liquids, which fluoresce strongly, and the matrix, which does not. The disruption of weak bonding effected by thermal treatment, which increased the

extract yield, was paralleled by changes in fluorescence intensity. The fluorescence spectra of the extracts also reflect the compositional differences between the mobile phase and the solubilised coal network.

Based upon solubility in chloroform, the mobile phase is estimated to constitute 5-15% wt of the coal. Obviously, this amount will vary if other characterising solvents are used.

It is to be expected there will be a gradation in the manner in which the smaller molecules are associated with the network. This may involve both physical and chemical forces such as covalent bonds; dispersion forces; hydrogen bonding; and could involve physical entrapment. It is doubtful whether any single technique can distinguish between these different modes of attachment sufficiently clearly to establish a precise boundary. Different energies will be required to disrupt the different types of attachment. It may be significant that Brown and Waters (16) found that the increase in chloroform-soluble yield upon coal preheating was dependent upon the pretreatment temperature. A minor peak in the yield was observed at temperatures in the region of 300°C and a second major one at 400-450°C.

The particular experimental studies, which have been described here, have provided a basis for a practical definition of the boundary of the mobile phase in coals and some tentative clues to the nature of its association with the network. Inevitably, other research techniques will provide a different perspective.

Acknowledgement

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Table 1. Coal Properties

Penn State Sample Bank No.	PSOC-1403	PSOC-1266	PSOC-1168	PSOC-1510
Seam	Anderson	L. Kittanning	L. Kittanning	L. Kittanning
County	Campbell	Mahoning	Lawrence	--
State	Wyoming	Ohio	Pennsylvania	Pennsylvania
ASTM rank	sub B	hvAb	hvAb	hvAb
Mean maximum reflectance of vitrinite (%)	0.40	0.83	0.83	0.89
Moisture (a.r. wt%)	23.3	3.4	2.4	1.4
Mineral Matter (a)	--	--	--	--
(dry, wt%) (c)	11.9	6.1	14.5	7.2
Elemental Composition (% dmmf)				
Carbon	72.9	83.2	71.8	77.4
Hydrogen	4.5	5.0	4.9	4.9
Oxygen (b)	20.4	8.6	18.8	15.2
Nitrogen	1.2	2.1	1.6	1.7
Organic sulfur	0.9	0.5	2.9	0.8
Petrographic Composition (Mineral-Free, vol %)				
Vitrinite	88	91	88	83
Exinite	2	3	4	10
Inertinite	11	6	7	7

(a) reported as ASTM ash

(b) by difference

(c) by low-temperature ashing

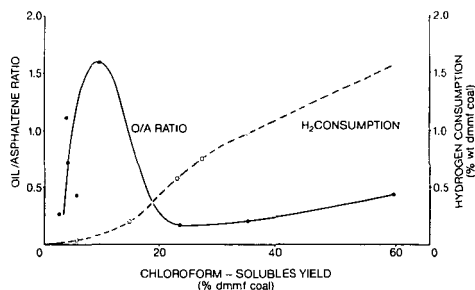


Figure 1. RELATIONSHIP OF H₂ CONSUMPTION AND O/A RATIO FOR hvAb COAL, PSOC-1266 (solvent-free hydrogenation; 400°C; 1% wt sulfided Mo; 7 MPa H₂)

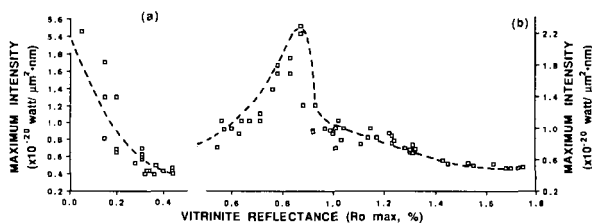


Figure 2. PRIMARY AND SECONDARY VITRINITE FLUORESCENCE (Absolute Units)
(a) PRIMARY FLUORESCENCE IN U-V IRRADIATION
(b) SECONDARY FLUORESCENCE IN BLUE-LIGHT IRRADIATION

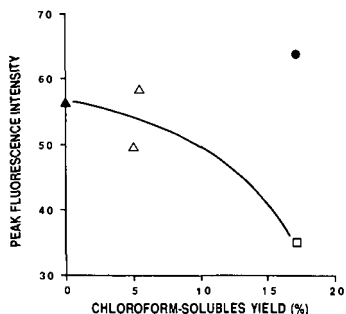


Figure 3. PEAK FLUORESCENCE INTENSITY OF RAW (▲) AND EXTRACTED VITRINITES (△) VERSES YIELD OF CHLOROFORM-EXTRACTABLES.
Also shown are data for thermally pretreated vitrinite before (●) and after (□) prolonged chloroform extraction (ref.6)

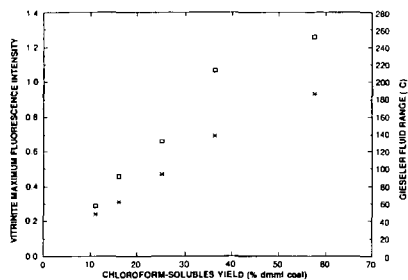


Figure 4. RELATIONS AMONG FLUORESCENCE INTENSITY, CHLOROFORM-SOLUBLES YIELD AND GIESELER PLASTICITY FOR HYDROGENATED COAL (PSOC-1510; solvent-free; 400°C; 5-60 min; 1% wt sulfided Mo; 7 MPa H₂ cold)

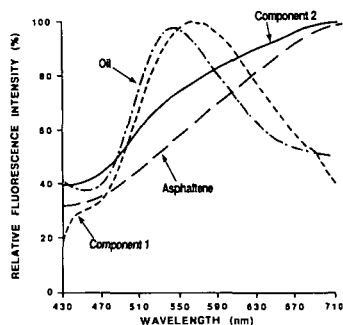


Figure 5. COMPARISON OF FLUORESCENCE SPECTRA OF TWO COMPONENTS IN CHLOROFORM-SOLUBLES FRACTION WITH OIL AND ASPHALTENE FRACTIONS OF HYDROGENATED COAL (PSOC-1266; solvent-free; 400°C; 60 min; 5% wt sulfided Mo; 7 MPa H₂ cold)

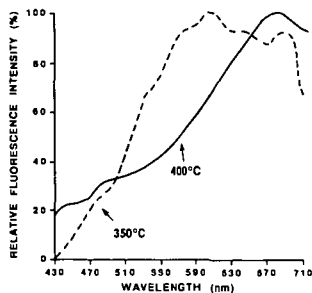


Figure 6. FLUORESCENCE SPECTRA OF VITRINITE FOLLOWING HYDROGENATION AT 350 AND 400°C (PSOC-1266; solvent-free; 60 min; 5% wt sulfided Mo; 7 MPa H₂ cold)